

Supporting Information

Rapid and ratiometric sensor for CAN (Ce^{4+}) through metal assisted oxidation reaction-altered Through Bond Energy Transfer (TBET): development of low cost devices (TLC plate sticks)

Shyamaprosad Goswami*, Sima Paul and Abhishek Manna

Department of Chemistry, Indian Institute of Engineering Science & Technology, Shibpur,
(Formerly Bengal Engg. and Science University, Shibpur), Howrah-711103, West Bengal,
India.

CONTENTS

1. Detection of Quantum yield.....	1
2. Calculation of the detection limit.....	2
3. Calculation of rate constant.....	3
4. pH effect on RCH moiety.....	3
5. $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and Mass spectra.....	3-5
6. UV-vis spectra of receptor with different oxidizing agents.....	6-8
7. Fluorescence spectra of receptor with different oxidizing agents.....	8-10
8. References.....	10

1. Determination of fluorescence quantum yield:

Here, the quantum yield ϕ was measured by using the following equation,

$$\phi_x = \phi_s (F_x / F_s)(A_s / A_x)(n_x^2 / n_s^2)$$

Where,

X & S indicate the unknown and standard solution respectively, ϕ = quantum yield,

F = area under the emission curve, A = absorbance at the excitation wave length,

n = index of refraction of the solvent. Here ϕ measurements were performed using quinine sulfate in ethanol as standard [$\phi = 0.546$] (error ~ 10%).

The quantum yield of **RCH** itself is 0.004 which is remarkably changed into 0.26, an enhancement around 65 fold is observed.

2. Calculation of the detection limit:

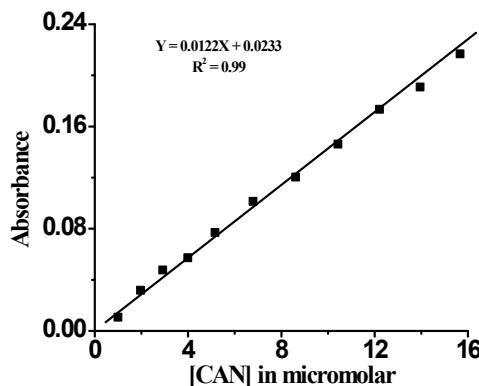


Figure S1: Absorbance change of RCH upon gradual addition of CAN.

The detection limit DL of **RCH** for CAN was determined from the following equation¹:

$$DL = K * S_{b1}/S$$

Where $K = 2$ or 3 (we take 2 in this case); S_{b1} is the standard deviation of the blank solution; S is the slope of the calibration curve.

From the graph we get slope = 0.0242, and S_{b1} value is 0.008292.

Thus using the formula we get the Detection Limit = 0.685 μM i.e. RCH can detect CAN in this minimum concentration.

3. Calculation of rate constant:

From the time vs. Fl. Intensity vs. time (sec.) plot at fixed wavelength (413nm) using first order rate equation (Figure S5), we get rate constant K = slope X 2.303 = 0.0495 X 2.303 = $11.39 \times 10^{-2} \text{ s}^{-1}$,

4. pH effect on RCH moiety:

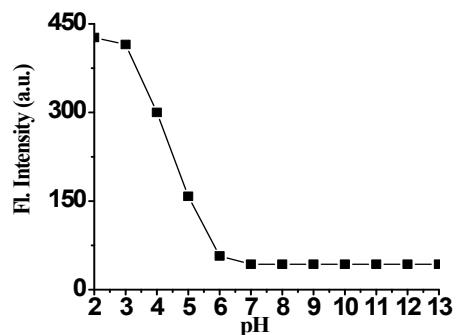
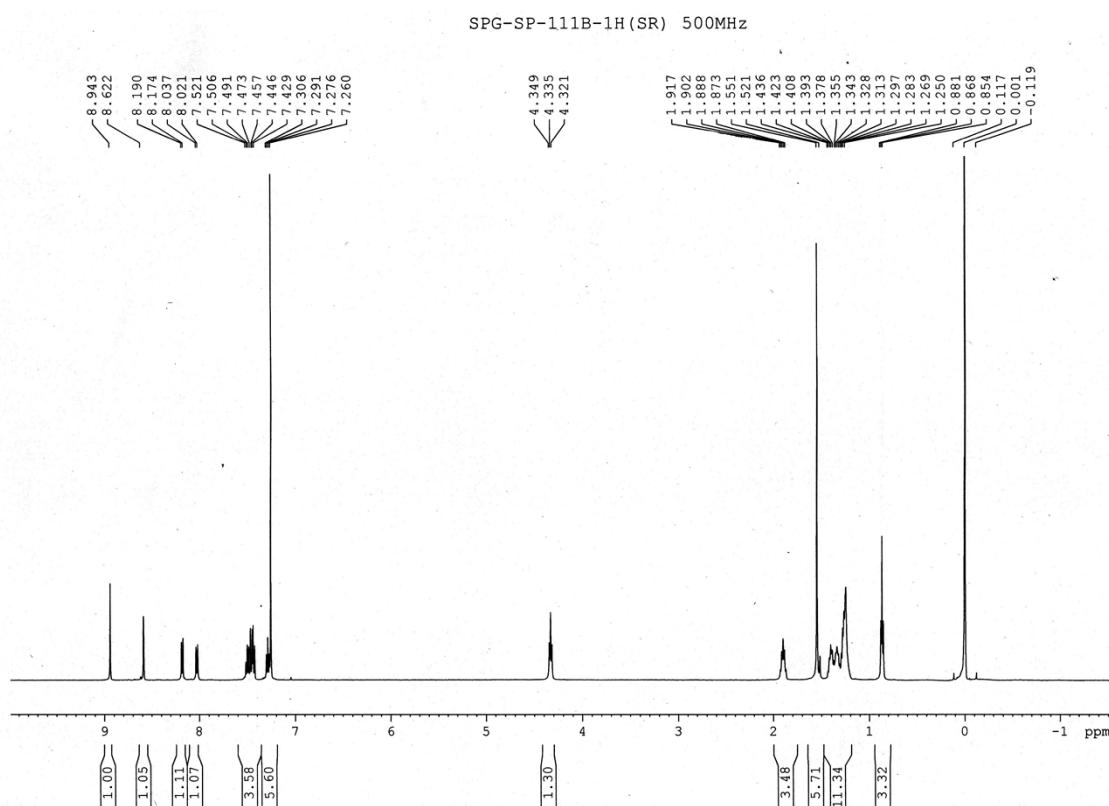


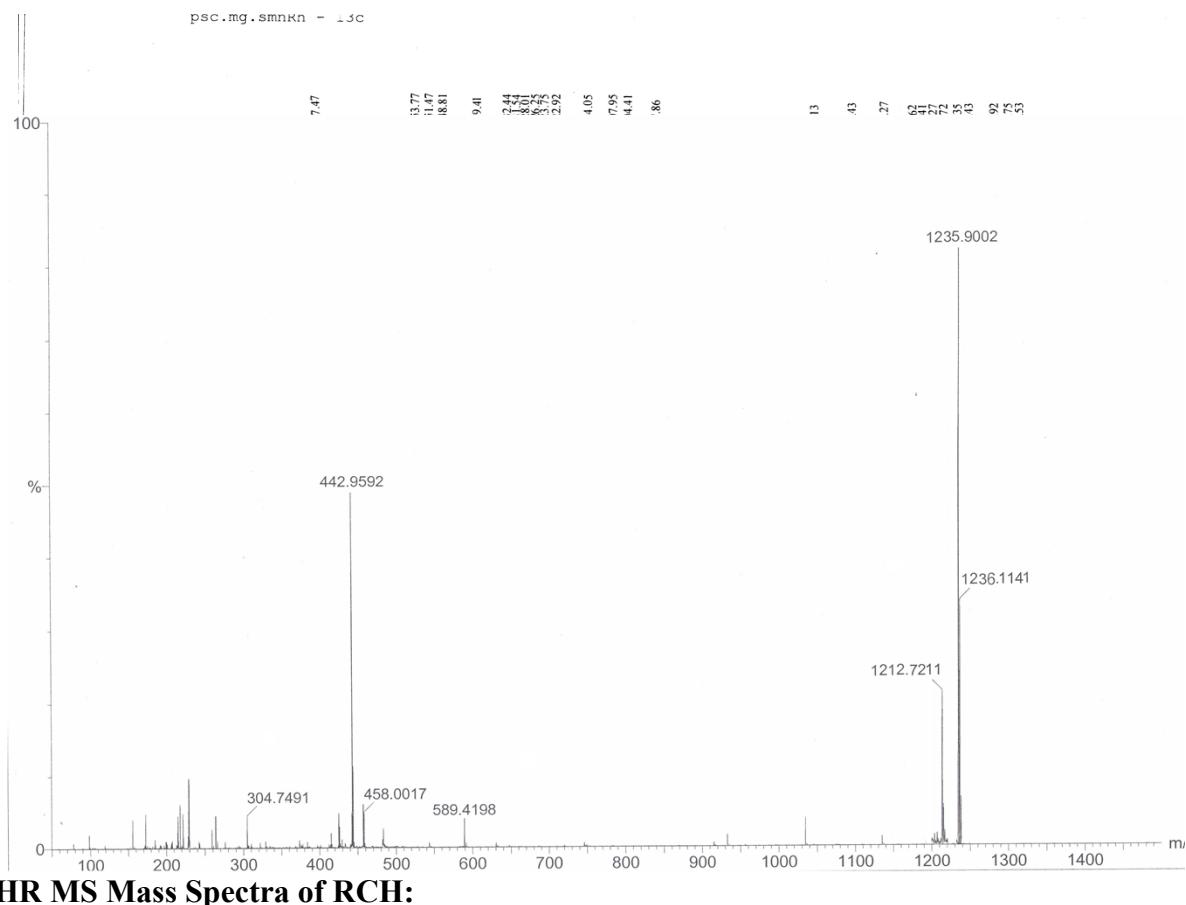
Figure S5: The change of fluorescence intensity of the receptor i.e. RCH ($c = 2 \times 10^{-5} \text{ M}$) (at 585 nm) with pH.

5. NMR and HRMS spectra of RCH and the corresponding CAN adduct:

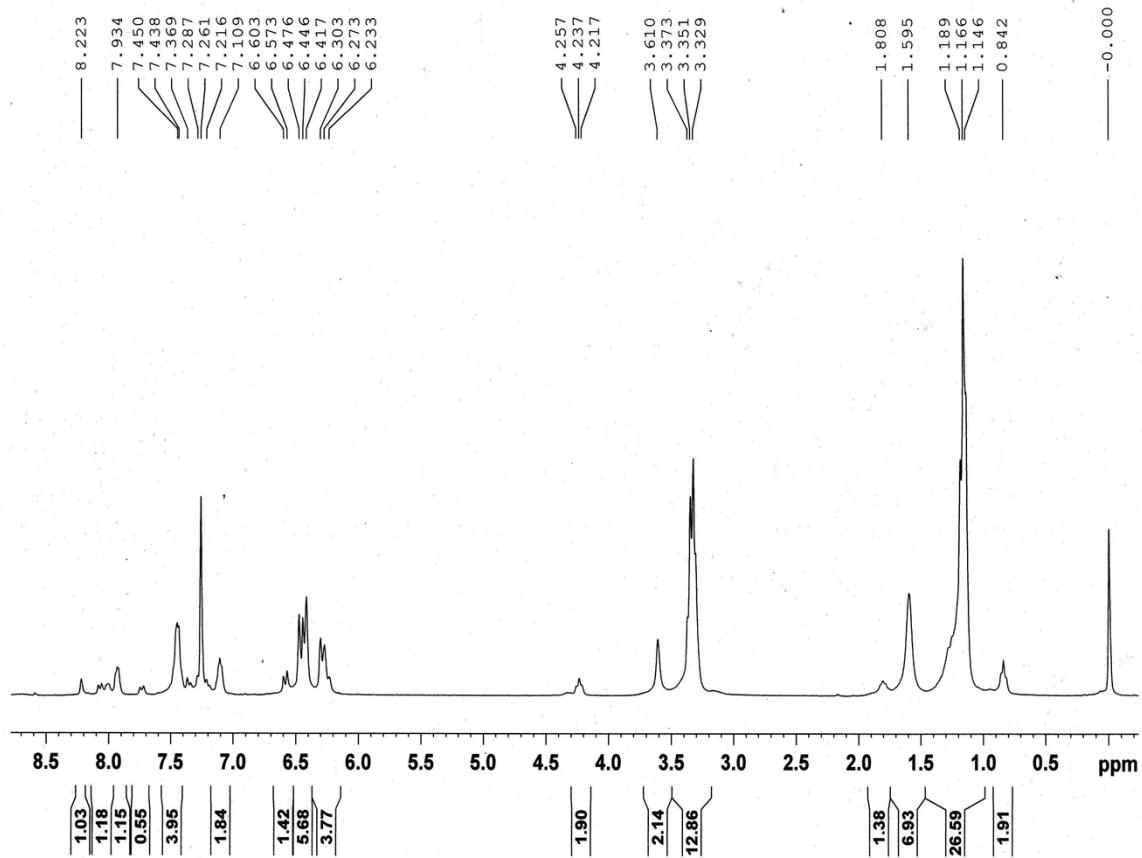
^1H NMR spectrum of Receptor i.e. RCH:



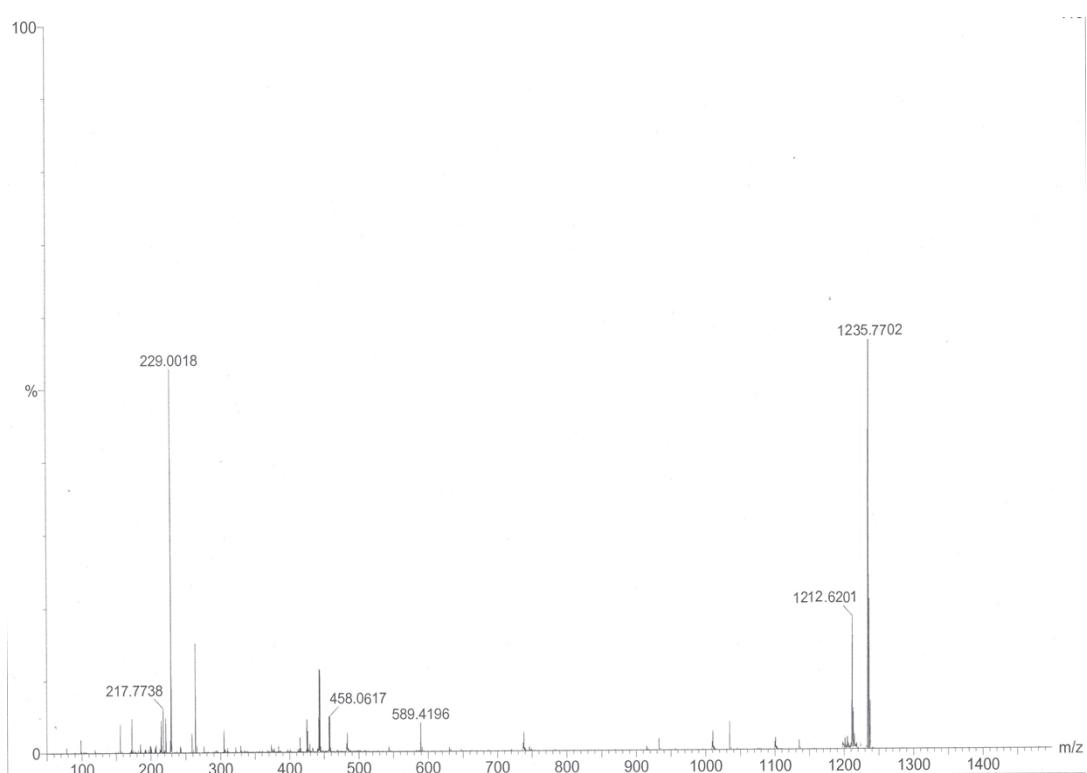
¹³C NMR spectrum of RCH:



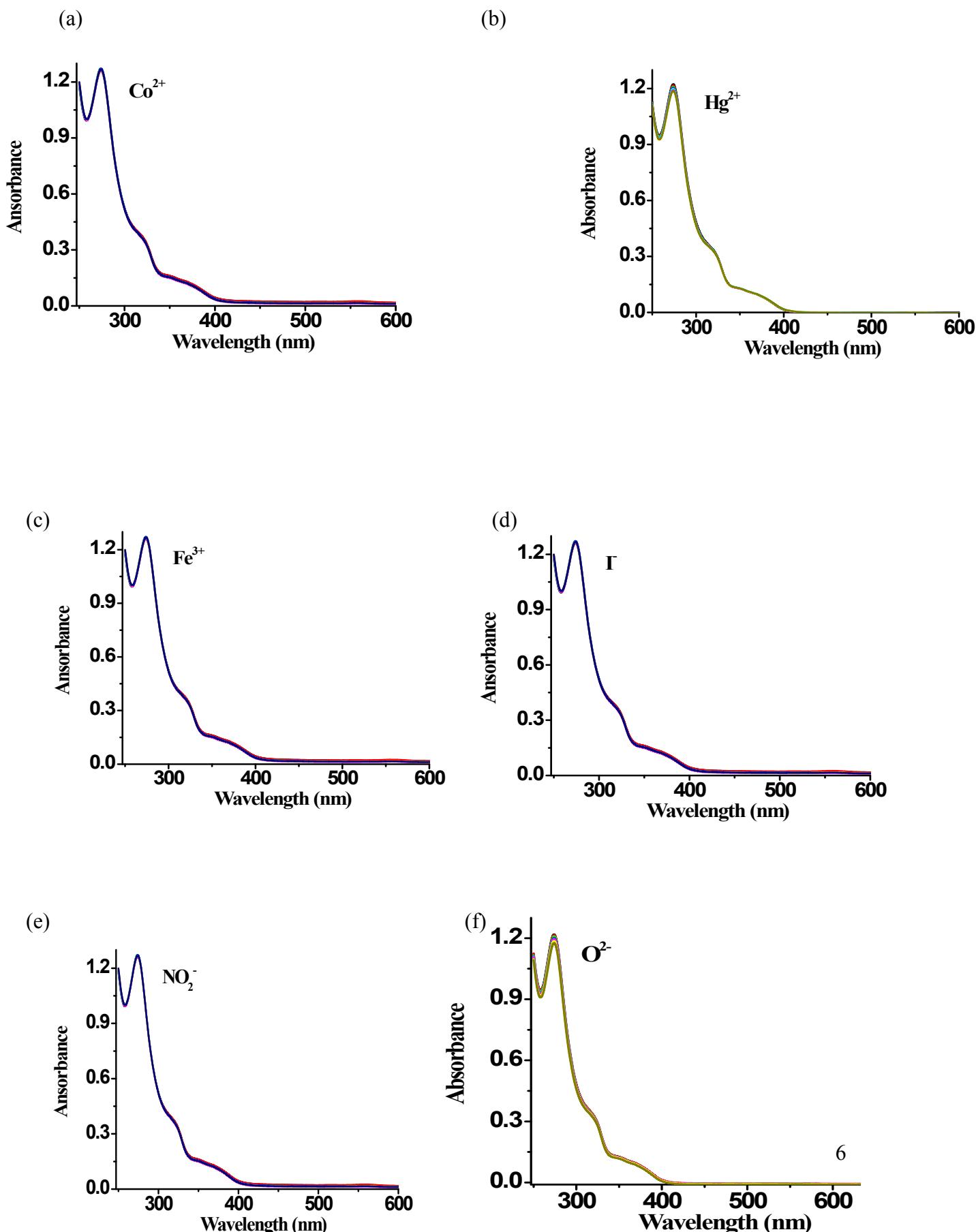
¹H NMR spectrum of CAN adduct:

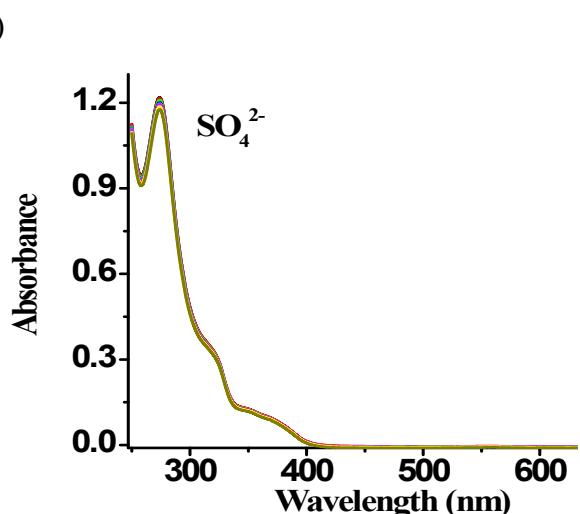
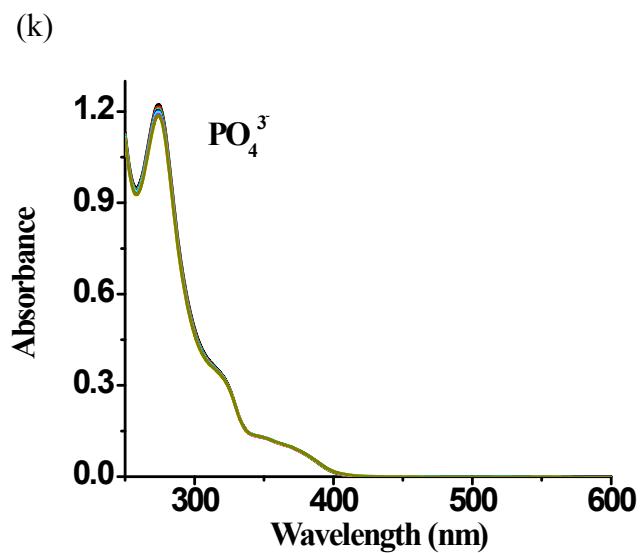
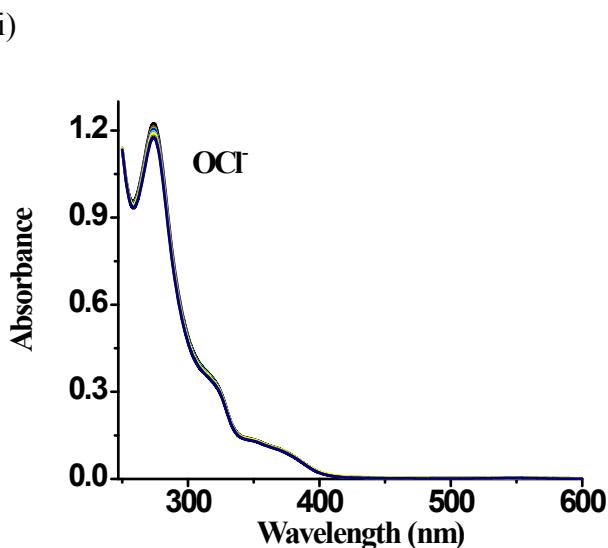
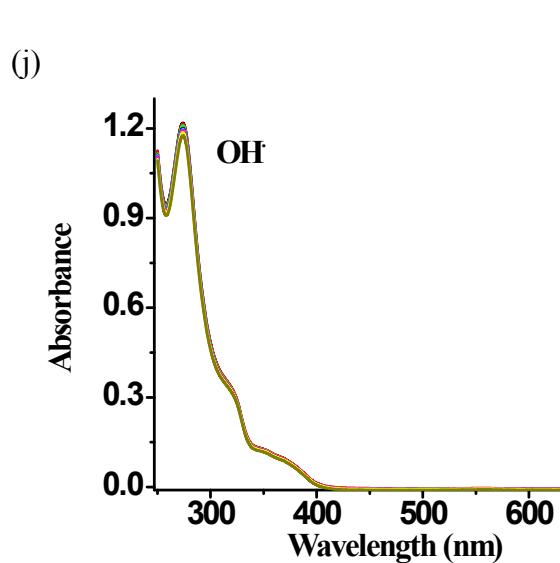
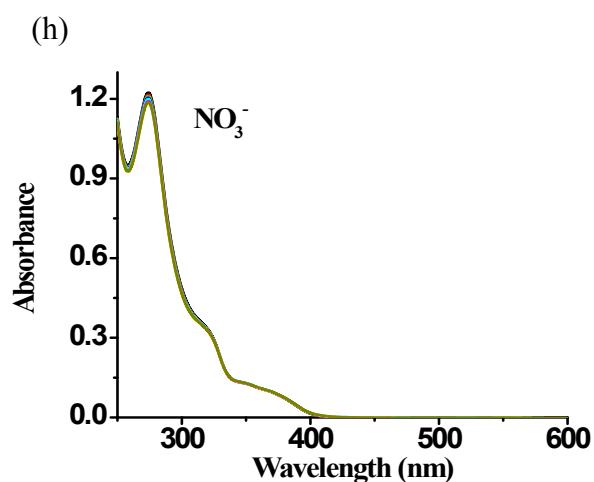
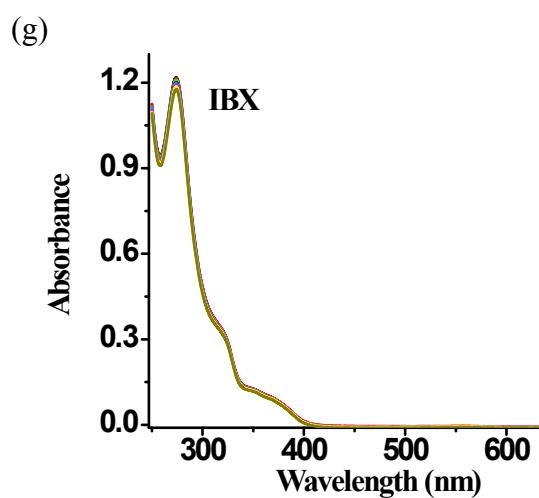


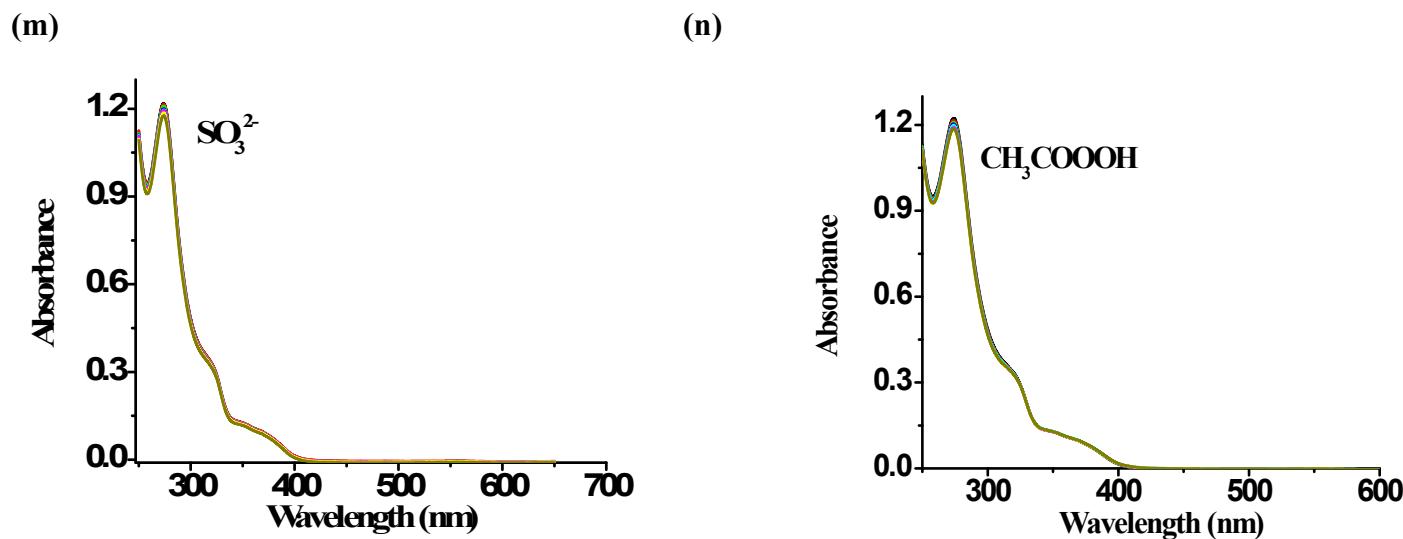
HR MS Spectra of CAN adduct :



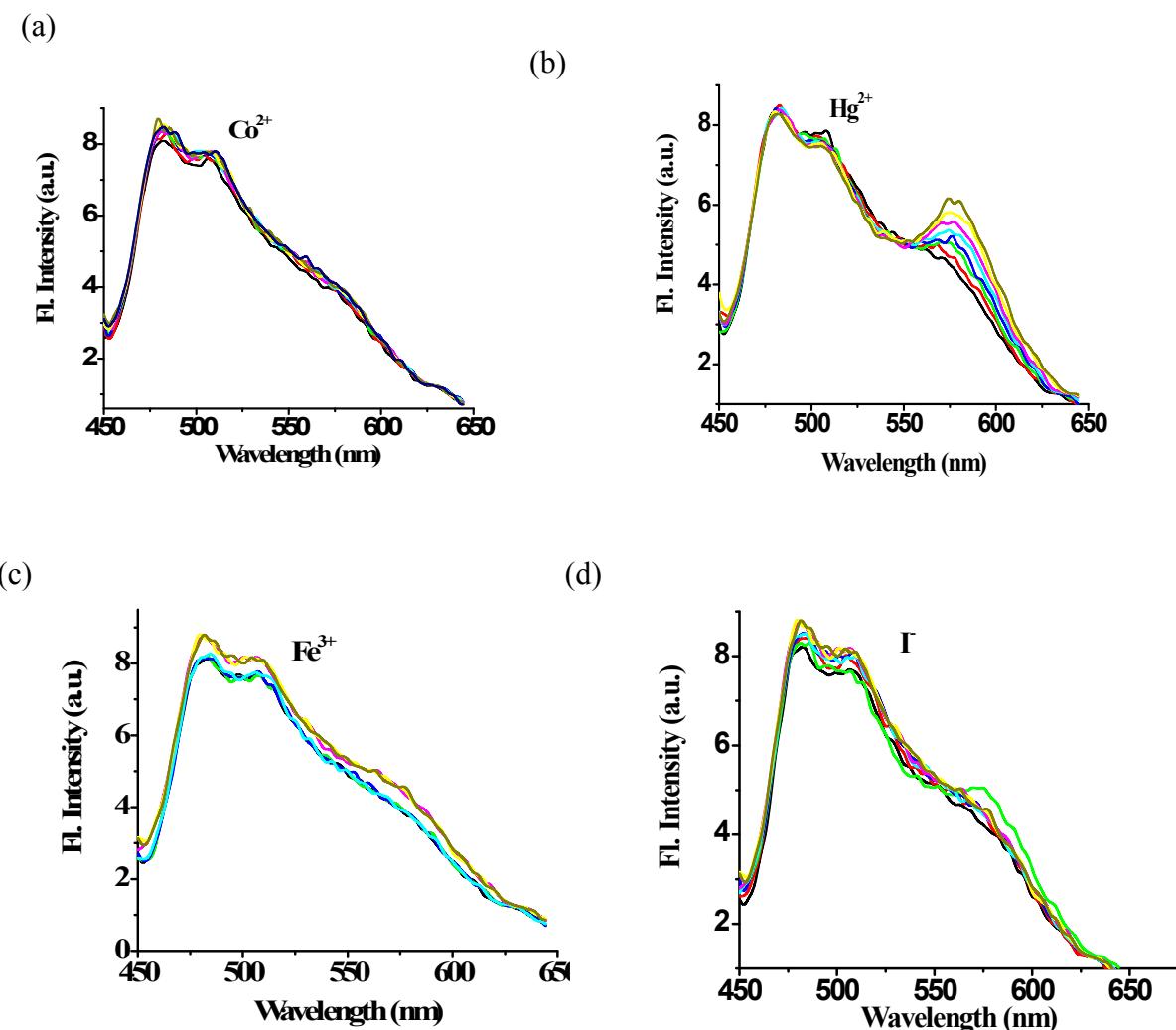
6. UV-vis absorption spectra of RCH with different oxidizing agents Co^{2+} , Hg^{2+} , Fe^{3+} , I^- , IBX, NO_3^- , NO_2^- , O_2^- , OH^- , OCl^- , PO_4^{3-} , SO_4^{2-} , SO_3^{2-} , $\text{CH}_3\text{CO}_3\text{H}$. The solutions of anions and oxidants were prepared from FeCl_3 , $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, HgCl_2 , KI , NaNO_2 , NaNO_3 , Na_3PO_4 , Na_2SO_3 , Na_2SO_4 in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$)

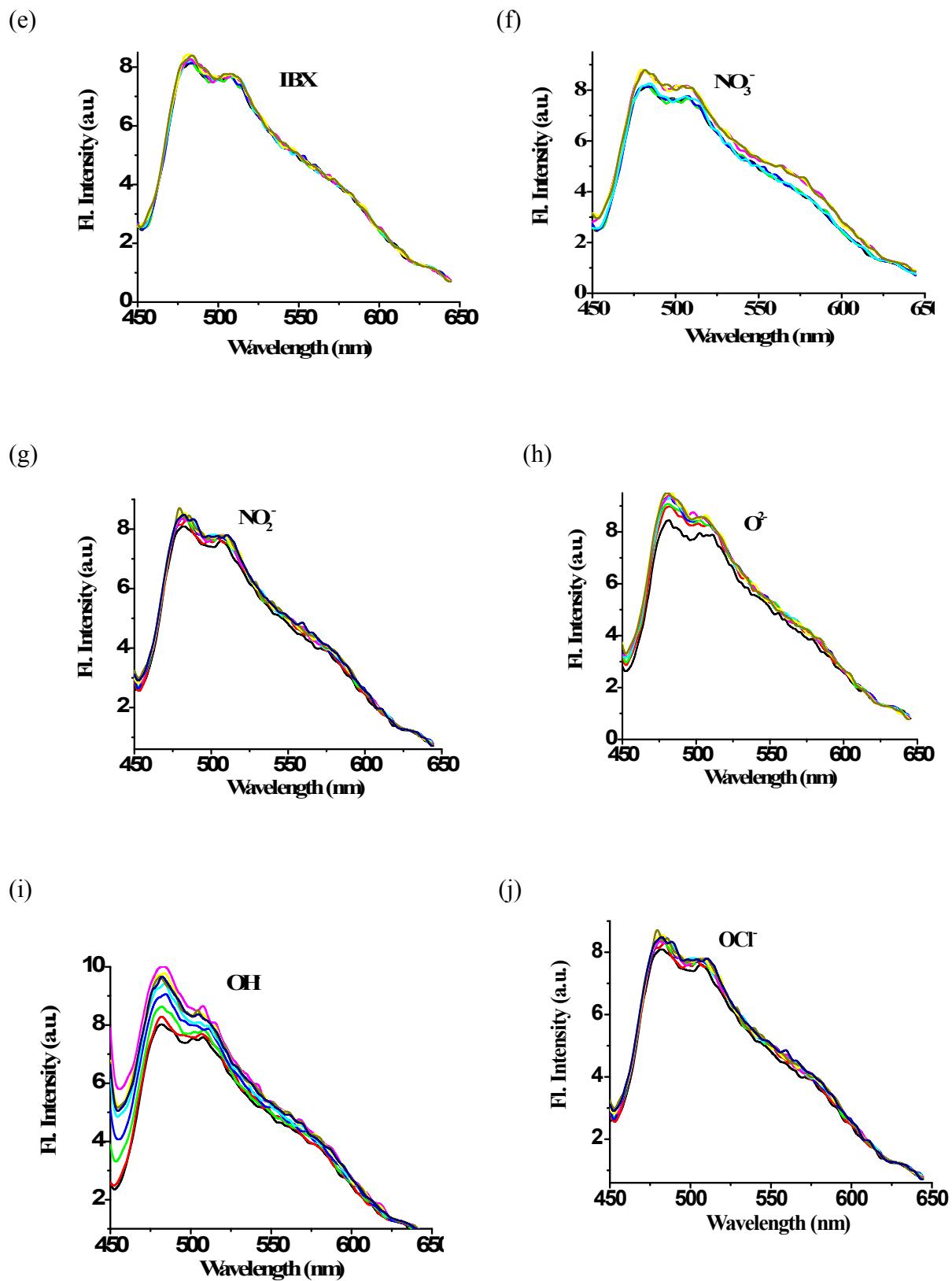


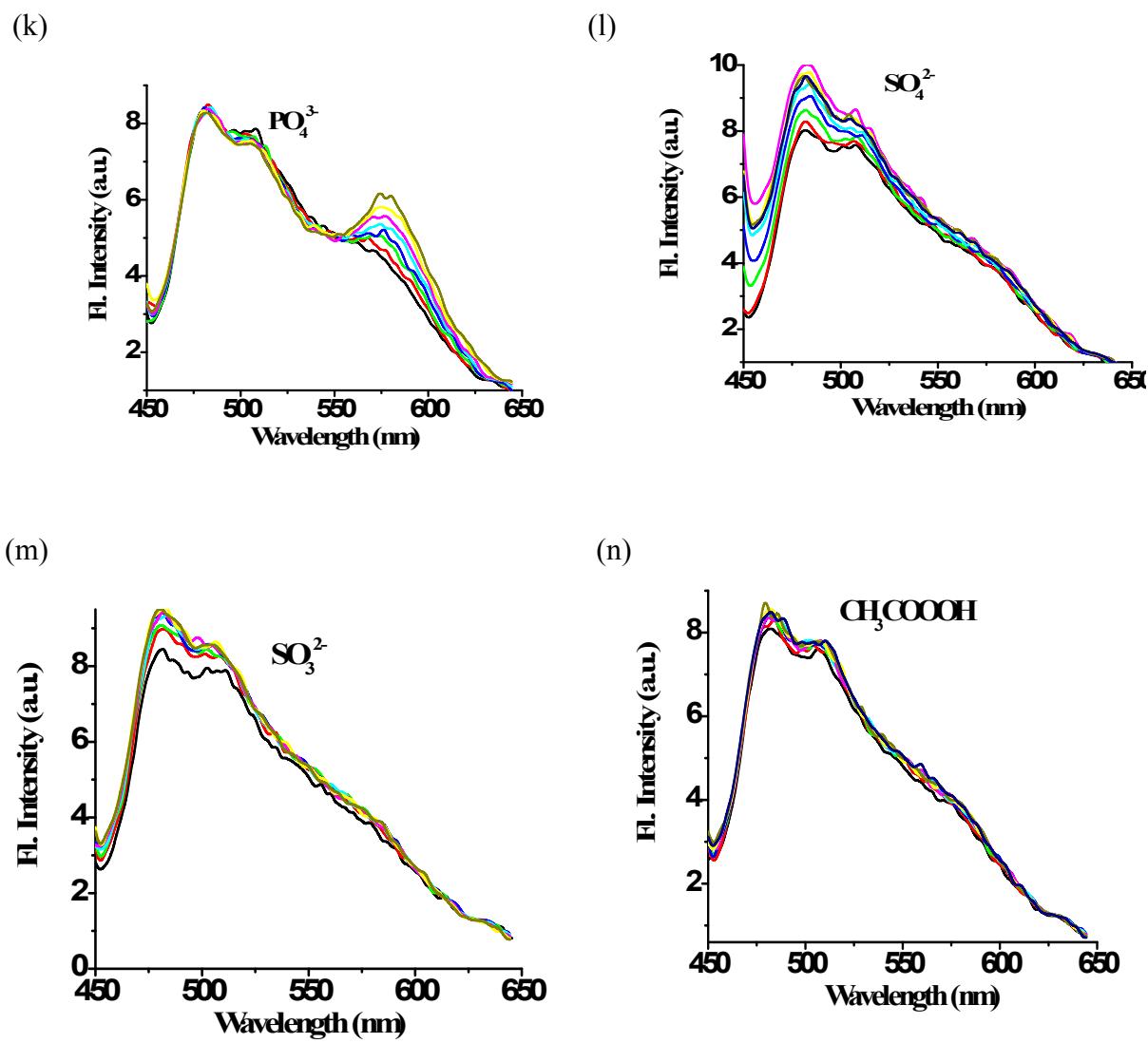




7. Fluorescence emission spectra of RCH with different oxidizing agents Co^{2+} , Hg^{2+} , Fe^{3+} , Γ , IBX, NO_3^- , NO_2^- , O_2^- , $\text{OH}\cdot$, $\text{OCl}\cdot$, PO_4^{3-} , SO_4^{2-} , SO_3^{2-} , $\text{CH}_3\text{CO}_3\text{H}$. The solutions of anions and oxidants were prepared from FeCl_3 , $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, HgCl_2 , KI , NaNO_2 , NaNO_3 , Na_3PO_4 , Na_2SO_3 , Na_2SO_4 in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$)







8. References :

1. M. Zhu, M. Yuan, X. Liu, J. Xu, J. Lv, C. Huang, H. Liu, Y. Li, S. Wang, D. Zhu, *Org. Lett.* 2008, **10**, 1481-1484